(19) Japan Patent Office (JP)

(12) Publication of Patent Application (A)

(11) Publication Number of Patent Application: Hei 3-231954

(43) Date of Publication of Application: October 15, 1991

(51) Int. Cl.[5] Identification Number

C 08 L 33/12 LJB

B 29 C 45/00

G 02 B 5/02 B

//(C 08 L 33/12

25:02)

Intraoffice Reference Number

8016-4J

2111-4F

7542-2H

Request for Examination: not made

Number of Claims: 5 (7 pages in total)

(54) Title of the Invention: ACRYLIC RESIN COMPOSITION FOR MOLDED BODY, MOLDED PRODUCT AND PRODUCTION METHOD FOR SAME

(21) Application Number: Hei 2-29078

(22) Application Date: February 7, 1990

(72) Inventor: Seiichi KAWANAMI

c/o Kuraray Co., Ltd.

2-28, Kurashiki-cho, Nakajo-machi,

Kitakambara-gun, Niigata

(72) Inventor: Yoshiro SUZUKI

c/o Kuraray Co., Ltd.
9-1, Hacchobori 2-chome, Chuo-ku, Tokyo
(72) Inventor: Yasutaro ITO
c/o Kuraray Co., Ltd.
2-28, Kurashiki-cho, Nakajo-machi,
Kitakambara-gun, Niigata
(72) Inventor: Yuji ANNAKA
c/o Kuraray Co., Ltd.
2-28, Kurashiki-cho, Nakajo-machi,
Kitakambara-gun, Niigata
(71) Applicant: Kuraray Co., Ltd.
1621, Sakazu, Kurashiki-shi, Okayama
(74) Agent: Patent Attorney, Ken HONDA

SPECIFICATION

1. Title of the Invention

Acrylic resin composition for molded body, molded product and production method for same

2. Claims

(1) An acrylic resin composition for a molded body comprising from 1 to 20 parts by weight of cross-linked polymer fine particles having an average particle diameter of from 1 to 15 μm comprising from 50 to 99% by weight of an aromatic vinyl monomer and from 1 to 50% by weight of a cross-linkable monomer on the basis of 100 parts by weight of a methyl

methacrylate type polymer.

(2) The resin composition according to Claim 1, wherein the cross-linked polymer fine particles are such fine particles as having an average particle diameter of from 5 to 9 μm which comprises particles each having a particle diameter of less than 10 μm by 60% or more in the weight distribution.

(3) An acrylic resin molded product comprising the acrylic resin composition according to Claim 1 or 2.

(4) A diffusion plate for an optical apparatus comprising a molded product according to Claim 3.

(5) A method for producing an acrylic resin molded product, which obtains an acrylic resin molded product having a light diffusion property and a matting property by injection-molding an acrylic resin material, being characterized by allowing the acrylic resin composition according to Claim 1 or 2 to be injection-molded in a cavity of a molding die which has not been subjected to a matting treatment.

3. Detailed Description of the Invention

[Industrial Field of Application]

The present invention relates to an acrylic resin composition for a molded body, a molded product and a method for producing same and, particularly, to an acrylic resin composition for a molded body which is excellent in a light diffusion property and a matting property, an acrylic resin

molded product, which has been prepared by injection-molding or extrusion-molding the composition, having a high light diffusion property and an excellent matting property and a production method therefor.

[Prior Art]

Acrylic resins have been used in various types of applications which require a light diffusion property such as a lamp cover, a display and a sign board. As for these acrylic resins each having the light diffusion property, (a) a product in which inorganic fine powder of barium sulfate, calcium carbonate, titanium oxide or the like having an average particle diameter of 10 μm or less is allowed to be contained in an acrylic resin (JP-A-60-139758), (b) a product in which transparent fine particles of silica, glass, aluminum hydroxide or the like of from 4 to 50 μm are allowed to be dispersed in an acrylic resin (JP-A-60-184559 and 61-4762) and (c) a product in which a styrene type resin or a cross-linked styrene-alkyl acrylate type polymer having a particle diameter of from 30 to 500 μm is mix-dispersed in an acrylic resin (JP-A-56-36535 and 61-159440) and the like have been known.

[Problems that the Invention is to Solve]

However, in a case of the acrylic resin containing the inorganic fine particles as in the method as described in the above-described item (a) or (b), there is a drawback in that, when the light diffusion property is tried to be sufficiently

enhanced, light ray transmittance is deteriorated. Further, in a case of the styrene type resin or the acrylic resin containing the cross-linked styrene-alkyl acrylate type polymer having a particle diameter of from 30 to 500 μm as in the method as described in the above-described item (c), there is a drawback in that, although a light diffusion effect is exhibited, the light ray transmittance is also deteriorated for realizing a perfect diffusion, a defect in an appearance of a molded product such as a diffusion defect or a flowing pattern is generated or matted state on the surface is not sufficient and, then, it was an actual state that requirements from a market which requires for a high light ray transmittance and a high light diffusion effect can not fully be responded to. Particularly, in the light diffusion plate for the optical apparatuses such as an OA apparatus, a liquid crystal display, a backlight panel and the like, there are strong requirements for improvements of the light ray transmittance and the light diffusion property.

Therefore, an object of the present invention is to solve these problems and to provide a matting acrylic resin molded product having a high light diffusion property close to a perfect diffusion.

[Means for Solving the Problems]

The present inventors have exerted intensive studies on types of light diffusion agents for solving the above-described

problems and, as a result, found that it is effective to blend cross-linked polystyrene polymer fine particles having a specified particle diameter to a methyl methacrylate type polymer, to thereby achieve the present invention.

Namely, according to the present invention, the above-described object is attained by an acrylic resin composition for a molded body containing from 1 to 20 parts by weight of cross-linked polymer fine particles having an average particle diameter of from 1 to 15 μm composed of from 50 to 99% by weight of an aromatic vinyl monomer and from 1 to 50% by weight of a cross-linkable monomer on the basis of 100 parts by weight of methyl methacrylate type polymer and an acrylic resin molded product containing the acrylic resin composition.

Further, at the time of obtaining an acrylic resin molded product by injection-molding an acrylic resin material, the above-described object can be attained by injection-molding the above-described acrylic resin composition in a cavity of a molding die which has not been subjected to a matting treatment.

Hereinafter, the present invention will be described in detail.

The term "methyl methacrylate type polymer" as used herein means a methyl methacrylate homopolymer or a copolymer containing methyl methacrylate by 80% or more and there is no

problem even when a minute additive such as an ultraviolet ray absorbing agent, a heat stabilizer, a colorant or inorganic fine particles are added within a range of the object. Further, a molecular weight thereof is not particularly limited in the present invention and, from the reason of facilitation of kneading at the time of injection-molding or extrusion-molding, physical properties or the like, is ordinarily from 50000 to 500000 and, preferably, from 70000 to 300000.

The cross-linked polymer fine particles according to the present invention are such fine particles as can be obtained by polymerizing an aromatic vinyl monomer and a cross-linkable monomer and can be blended with any one of other copolymerizable monomers within a range which does not give an adverse effect to the object of the present invention.

As for aromatic vinyl monomers, styrene, α-methyl styrene, vinyl toluene, halogenated styrene and the like can be used and, thereamong, styrene is particularly preferred. An amount of the aromatic vinyl monomer to be used is in the range of from 50 to 90% by weight and, preferably, from 80 to 95% by weight.

As for cross-linkable monomers, a compound having two unsaturated bonds or more in a molecule is used. As for specific examples of such compounds, difunctional dimethacrylates such as ethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, 1,4-butanediol

dimethacrylate and neopentyl glycol, and polyvalent vinyl benzenes such as divinyl benzene are advantageously mentioned and, thereamong, divinyl benzene is particularly preferred. An amount of the cross-linkable monomer to be used is, based on the weight of the monomer, in the range of from 1 to 50% by weight and, preferably, from 5 to 20% by weight.

A particle diameter of each of the above-described fine particles is in the range of from 1 to 40 μm, preferably from 1 to 25 μm and, most preferably, from 1 to 10 μm and an average particle diameter thereof is in the range of from 1 to 15 μm and, preferably, from 5 to 9 μm. In regard to a preferable aspect of the fine particles, from the standpoint of the light diffusion properties against variations of contents depending on difference of particle diameters of polymer fine particles and an influence to the matted surface appearance, particles each having a particle diameter of less than 10 μm occupy 60% or more and, preferably, 90% or more in the weight distribution within the above-described ranges. The term "average particle diameter" as used herein means a particle diameter which falls on a point showing 50% of an entire weight obtained by weight-integrating respective particle diameters and can, for example, be determined in accordance with a gravitational liquid sedimentation method by using a light ray transmittance type particle size distribution measuring apparatus (trade name: SKA 5000; available from Seishin Enterprise Co., Ltd.)

or the like. From the spherical standpoint of uniformity of a light diffusion state and a texture, spherical fine particles prepared by suspension-polymerization are favorably used and those having a narrower particle size distribution are favorably used since uniform light diffusion properties can be obtained. As for such fine particles prepared by the suspension-polymerization, those which are produced by prescriptions as described in JP-A-64-26617, 1-146910, 1-172412 and the like or, as those which are available in the market, Techpolymers SBX-4, SBX-6, SBX-8, SBX-12 and the like (cross-linked polystyrene tiny globular fine particles; available from Sekisui Plastics Co., Ltd.) can be used. When the particle diameter of the polymer fine particles is less than 1 μm, the polymer fine particles tends to appear reddish by transmitted light, which is not favorable, while, when the particle diameter of the polymer fine particles is more than 40 μm, or an average particle diameter thereof is more than 15 μm, it is difficult to obtain a light diffusion property close to a perfect diffusion, which is not favorable. Further, an amount of the fine particles to be blended is, based on 100 parts by weight of methyl methacrylate type polymer, in the range of from 1 to 20 parts by weight and, preferably, from 3 to 10 parts by weight. When the amount to be blended is less than 1 part by weight, it tends to be transparent and a sufficient light diffusion property can not be obtained and,

also, a matted state of the surface thereof is not sufficient, while, when it is more than 20 parts by weight, the light ray transmittance is deteriorated and, even when it is added more than this level, the matting effect, the light diffusion property and the like can not be expected to be further enhanced, which is not favorable.

In the thus-obtained cross-linked polymer fine particles, it is preferable that a value of a gel content is 95% or more and a degree of swelling is 2 or less from the purpose of obtaining a sufficient light diffusion property. When the gel content is less than 95% or the degree of swelling is more than 2, the particle diameter of the particle at the time of kneading is varied and not only the diffusion property close to the perfect diffusion can not be obtained, but also the matted surface appearance can not be uniform nor fine, which is not favorable.

Adjustments of the gel content and the degree of swelling of the cross-linked polymer can be performed by adjusting types and volumes of cross-linkable monomer and by using a chain transfer agent but, by an ordinarily performed suspension-polymerization, the cross-linked polymer fine particles having a gel content of 95% or more and a degree of swelling of 2 or less can be obtained.

The term "acrylic resin composition for a molded body excellent in a light diffusing property and a matting property"

as used herein means an article which contains, based on 100 parts by weight of methyl methacrylate type polymer, from 1 to 20 parts by weight of the cross-linked polymer fine particles and means, for example, an article in which a methyl methacrylate polymer and the above-described fine particles are stir-mixed by a Henschel mixer or the like or are mixed with each other and, then, the resultant mixture is subjected to an extruder to be formed in a pellet state or the like. In order to allow the above-described composition to be stably stored or to be easily processed by a molding machine, the composition in pellet form is favorably used. Such acrylic resin composition for the molded body as described above is used as a material for a molded body for extrusion-molding, injection-molding or the like. In a case of the extrusion-molding, since matted state depends on a contact state with a forming roll after the resin is extruded, the composition is favorable for such injection-molding causing no problem and is favorably used as an acrylic resin composition for the molded body which is suitable for the injection-molding and is excellent in the light diffusion property and the matting property.

Injection-molding conditions according to the present invention are not essential requirements for the present invention and an acrylic resin molded product excellent in the light diffusion property and the matting property can be

produced by injection-molding the above-described acrylic resin composition in a die cavity which has not been subjected to a matting treatment by using an ordinary injection-molding machine under ordinary injection conditions. For example, the above-described methyl methacrylate polymer and the above-described fine particles are stir-mixed by using a Henschel mixer or the like or are mixed with each other and, then, the resultant mixture is subjected to an extrusion-molding machine to be formed in a pellet state and, thereafter, the mixture or such pellets are injection-molded in a cavity of a molding die having a mirror surface by the injection-molding machine, to thereby obtain an acrylic resin molded product having a diffusion property close to a perfect diffusion and a uniform beautiful matted surface which can not be obtained by a conventional material.

(EXAMPLE)

Hereinafter, the present invention is specifically described with reference to embodiments.

All "percentages" and "parts" denoted in Examples and Comparative Examples are given by "percentages by weight" and "parts by weight", respectively. Further, a performance of an acrylic resin molded product and a gel content and a degree of swelling of a cross-linked polymer fine particles which were obtained in Examples and Comparative Examples were measured and evaluated by the methods as described below.

Light Ray Transmittance and Haze Value

Measurements were performed in conformity to JIS K7105 by using an integrating sphere type light ray transmittance measuring apparatus (trade name: RM-15; available from Murakami Color Research Laboratory), to thereby determine an entire light rays transmittance and a haze value.

Transmittance Characteristic

Transmittances at respective angles of 0°, 5°, 10°, 20°, 30°, 40°, 50°, 60°, 70°, 80° and 90° were measured by using a goniophotometer (trade name: GP-1R; available from Murakami Color Research Laboratory) under following optical conditions:

flux of light: 12 ϕm/m;

degree of parallelization: ±0.5 or less;

condenser lens: effective aperture: 16 m/m ϕ;

light-receiving visual angle: 0.86°;

light-receiving slit diameter: 3 m/m ϕ; and

spectral condition: approximate to CIE relative luminosity against C light.

Surface State

A fluorescent lamp was allowed to be reflected on a surface of a sample in a room and the reflected lamp was visually observed and, then, matted state of the sample was indicated by the following marks:

OO ··· an outline of a fluorescent lamp was not observed

at all and a uniform beautiful matted surface was given;

O ··· an outline of a fluorescent lamp was not observed at all or scarcely observed;

Δ ··· an outline of a fluorescent lamp was observed but obscure and there were irregularities on a surface;

X ··· an outline of a fluorescent lamp was clearly observed and there were scarcely irregularities on a surface; and

XX ·· a surface was rough and there was no uniformly matted state.

Transparency

A sample was placed in parallel at a position which is 8 cm in front of a striplight (trade name: Palux; available from Matsushita Electric Industrial Co., Ltd.) of 15 W and, further, a visual observation was conducted through the sample at a position which is at a distance of 50 cm from the sample as to whether the outline of the light source can be seen or not and, then, the results are indicated by the following marks:

O: an outline of a fluorescent lamp was not observed;

Δ: an outline of a fluorescent lamp was slightly observed; and

X: an outline of a fluorescent lamp was clearly observed.

Gel Content and Degree of Swelling

A given amount of a cross-linked polymer fine particles was weighed in a weighing bottle and, then, dipped in methyl ethyl ketone (MEK) having an amount of about 100 times the

amount thereof for 48 hours. After dipping, an excess amount of MEK was sufficiently removed by decantation and, then, a weight of a sample which has been swelled with MEK was determined. Thereafter, MEK was removed from the sample by drying the sample under reduced pressure, to thereby determine a bone-dry weight of the sample. Being based on the thus-determined bone-dry weight, the gel content and the degree of swelling were calculated by the respective following formulae:

Gel content (wt%)=[bone-dry weight(after dipping in MEK)/weight of collected sample]x100; and

Degree of Swelling=[(weight of sample swelled with MEK)-(bone-dry weight)]/ bone-dry weight.

Example 1

18.37 g of polyvinyl alcohol (trade name: PTA 420; available from Kuraray Co., Ltd.) as a suspension-dispersing agent was dissolved in 2625 ml of distilled water in a separable flask of 5-liter capacity and, then, the resultant solution was added with a solution containing 540 ml of styrene as a monomer system, 60 ml of divinyl benzene, 400 ml of toluene and 1200 g of lauloyl peroxide. The resultant mixture was allowed to be dispersed by using a lab-disperser (type: X-1020; available from Mitamura Riken) until a largest particle came to have a particle diameter of 25 μm while observing it under a microscope. The flask was, then, equipped with a

thermometer, a stirrer and a cooling pipe and, thereafter, the resultant dispersion was subjected to a polymerization reaction under a flow of nitrogen for 6 hours at 80°C. The resultant slurry was subjected to a suction filtering and, then, fine particles thus filtered out were again dispersed in distilled water to rinse an attached polyvinyl alcohol and, then, filtered. Thereafter, the article thus filtered out was dried in vacuum at a temperature of 100°C for 2days to evaporate toluene as a diluent and, when a particle diameter thereof was measured by using a transmittance type particle size distribution measuring apparatus (trade name: SKA5000; available from Seishin Enterprise Co., Ltd.), cross-linked polymer fine particles having a particle diameter of from 2 to 25 μm and an average particle diameter of 8 μm (particles of less than 10 μm occupy 65% in the weight distribution) were obtained. A gel content and a degree of swelling of these fine particles were 98% and 1 or less, respectively. The thus-obtained fine particles were added to the methyl methacrylate polymer containing 5% of methyl acrylate (trade name: PARABEADS; available from Kuraray Co., Ltd.) at a rate of 5 parts against 100 parts of the polymer and are subjected to stir-mixed by using a Henschel mixer. The resultant mixture was extruded to be in pellets by an extruder (trade name: VSK-40; available form Chuo Kikai Seisakusho) and, then, the pellets were injection-molded in a cavity having a mirror

surface under conditions of a molding temperature of from 200 to 240°C and a metallic die temperature of 50°C by using an injection-molding machine (trade name: IS-25Zp; available from Toshiba Machine Co., Ltd.), to thereby obtain a planar molded product having a thickness of 2 mm.

Results of performance evaluations of this molded product are shown in Table 1 and, on this occasion, an acrylic resin molded product having a high light diffusion property and a favorable matted surface was obtained.

Examples 2 to 4

Pelletization and injection-molding were performed in a same manner as in Example 1 except for adding cross-linked polymer fine particles having a composition and a particle diameter as described below at various amounts of addition, to thereby obtain a planar molded products each having a thickness of 2 mm. Results of performance evaluations of these molded products are shown in Table 1.

Example No.	Composition	Particle diameter
2	Styrene: 95 parts Divinyl benzene: 5 parts	Particle diameter: 1 to 10 μm; average particle diameter: 4 μm; particles of less than 10 μm: 97% in weight distribution
3	Same as above	Particle diameter: 1 to 16 μm; average particle diameter: 6 μm; particles of less than 10 μm: 91% in weight distribution; gel content: 96%; degree of swelling: 1.1
4	Same as above	Particle diameter: 2 to 64 μm; average particle diameter: 12 μm; particles of less than 10 μm: 30% in weight distribution

Comparative Examples 1 and 2

Pelletization and injection-molding were performed in

a same manner as in Example 1 except for adding cross-linked polymer fine particles having a composition and a particle diameter as described below at various amounts of addition, to thereby obtain a planar molded products each having a thickness of 2 mm. Results of performance evaluations of this molded product are shown in Table 1.

Comparative Example No.	Composition	Particle diameter
1	Styrene: 95 parts Divinyl benzene: 5 parts	Particle diameter: 2 to 64 μm; average particle diameter: 22 μm; particles of less than 10 μm: 5% in weight distribution
2	Same as above	Particle diameter: 12 to 200 μm; average particle diameter: 50 μm

In an article having an average particle diameter of 50 μm, when a filling speed of the resin was fast, not only a flowing pattern by large particles was apt to be appeared, but also a surface of the molded product did not have a uniform matted state and a light diffusion property was also inferior.

Comparative Example 3

Polystyrene fine particles having a particle size distribution of from 1.0 to 20 μm and an average particle diameter of 6 μm (particles of less than 10 μm is 90% in the weight distribution) were added to a methyl methacrylate polymer containing 5% of methyl acrylate at addition amounts of 1 part, 3 parts, 5 parts and 10 parts against 100 parts of polymer, respectively and, then, the resultant respective mixtures were mix-stirred by using a Henschel mixer, to thereby obtain respective planar molded products each having a

thickness of 2 mm in a same manner as in Example 1. Results of performance evaluations thereof are shown in Table 1 and, on this occasion, molded products each having a high diffusion and a high light ray transmittance was not able to be obtained and, further, when an amount of addition is small, the molded products have a diffusion deficiency, while, when the amount of addition was large, a sea-shell pattern was appeared thereon.

Comparative Example 4

0.5 part, 1 part, 5 parts and 10 parts of polystyrene fine particles (trade name: Techpolymer SB-10; available from Sekisui Plastics Co., Ltd.) having a particle distribution of from 3 to 30 μm and an average particle diameter of 10 μm were added to 100 parts of methyl methacrylate polymer which has been used in Comparative Example 3, respectively and, then, mix-stirred by using a Henschel mixer, to obtain planar molded products each having a thickness of 2 mm in a same manner as in Example 1. In these molded products, there was no molded product having a high diffusion and a high light ray transmittance and a diffusion deficiency and a sea-shell pattern was generated in a same manner as in Comparative Example 3.

No entry below.

Table 1

	Amount of fine particles to be blended (part)	Entire light rays transmittance (%)	Haze (%)	Transmittance characteristics: Angle distribution of transmittance light (% when direction at 0° is 100)						Surface state	Transparency	Remarks
				0°	10°	30°	40°	60°	70°			
Example 1	5	57	94	100	99	90	81	52	32	OO	O	
Example 2	1	71	95	100	96	69	53	27	16	Δ	O	
	3	57	94	ditto	99	90	81	52	32	O	O	
	5	48	ditto	ditto	ditto	92	84	55	34	OO	O	
	10	40	95	ditto	ditto	ditto	ditto	ditto	ditto	OO	O	
	30	39	94	ditto	ditto	ditto	ditto	54	ditto	OO	O	
Example 3	1	74	94	100	93	58	41	19	11	O	O	
	3	59	ditto	ditto	99	89	80	51	31	OO	O	
	5	55	93	ditto	ditto	92	83	54	34	OO	O	
	10	45	95	ditto	ditto	ditto	84	50	28	OO	O	
	30	30	94	ditto	ditto	ditto	83	52	31	OO	O	
Example 4	1	80	93	100	43	13	8	3	1	Δ	O	
	3	65	95	ditto	97	76	62	33	17	O	O	
	5	58	ditto	ditto	99	88	79	47	26	O	O	
	10	50	ditto	ditto	ditto	92	83	50	28	OO	O	
	30	37	94	ditto	ditto	ditto	82	ditto	ditto	OO	O	
Comparative Example 1	1	82	89	100	4	1	0	0	0	Δ	Δ	
	3	69	94	ditto	91	57	42	20	10	Δ	O	
	5	60	95	ditto	98	84	72	41	20	Δ	O	
	10	52	94	ditto	99	91	83	50	28	O	O	
	30	37	ditto	ditto	ditto	ditto	82	48	27	OO	O	
Comparative Example 2	1	86	65	100	0	0	0	0	0	X	X	
	3	79	90	ditto	10	2	1	0	0	XX	Δ	
	5	74	94	ditto	51	20	13	5	3	XX	O	
	10	64	96	ditto	96	71	57	30	15	XX	O	
Comparative Example 3	1	52	94	100	0	0	0	0	0	X	X	Presence of diffusion deficiency
	3	37	ditto	ditto	72	65	58	37	23	X	O	
	5	31	ditto	ditto	99	90	82	53	33	X	O	
	10	19	96	ditto	ditto	93	84	55	35	X	O	Presence of sea-shell pattern
Comparative Example 4	0.5	69	52	100	0	0	0	0	0	X	X	Presence of diffusion deficiency
	1	55	89	ditto	1	1	0	0	0	X	X	ditto
	5	30	94	ditto	99	92	84	53	30	X	O	Presence of sea-shell pattern
	10	21	ditto	ditto	ditto	93	86	55	31	X	O	ditto

[Advantage of the Invention]

As described above, since the present invention relates to the acrylic resin composition for the molded body which contains from 1 to 20 parts by weight of cross-linked polymer fine particles having an average particle diameter of from 1 to 15 μm composed of from 50 to 99% by weight of aromatic vinyl monomer and from 1 to 50% by weight of cross-linkable monomer on the basis of 100 parts by weight of a methyl methacrylate type polymer and is excellent in the light diffusion property and the matting property, the light diffusion property and the matted state can be varied depending on the particle diameter and an amount to be added of the polymer fine particles to be blended and, therefore, the compositions for the molded bodies having various types of light diffusion properties and matting properties can conveniently be provided and, particularly, are useful as injection-molding materials excellent in mass-productivity.

Further, since the present invention relates to the acrylic resin molded product which is molded by extrusion-molding or injection-molding the above-described acrylic resin composition for the molded body and is excellent in the light diffusion property and the matting property, it can not only be supplied in a large quantity and at low cost, but also be useful as a lamp cover, a display, a glazing, a measuring instrument cover and the like and is particularly favorable

as optical diffusion plates for optical apparatuses such as an OA apparatus, a liquid crystal display and a backlight panel which have rapidly been progressed in recent years.

Further, since the present invention relates to a method for producing the acrylic resin molded product which is molded by injection-molding the above-described acrylic resin composition in a cavity of a molding die and is excellent in the light diffusion property and the matting property, it is not necessary to perform delicate processing on a surface of a cavity or sufficiently polish to realize a mirror surface and, therefore, a metallic die can be produced at a low cost and, also, various types of molded products excellent in the light diffusion property and matting property can be produced in one metallic die by changing molding materials and, further, since the dispersion deficiency or the sea-shell pattern is not generated at all, the acrylic resin molded product which is excellent in the light diffusion property and the matting property can conveniently be provided at a low cost, which is advantageous.

4. Brief Description of the Drawing

FIG. 1 is a diagram showing respective transmittance characteristics of Example 1 (A), a case (B) in which an amount of fine particles in Example 2 to be blended is 3 parts, a case (C) in which an amount of fine particles in Example 3 to be blended is 3 parts, a case (D) in which an amount of fine

particles in Example 4 to be blended is 5 parts, a case (E) in which an amount of fine particles in Comparative Example 1 to be blended is 5 parts and a case (F) in which an amount of fine particles in Comparative Example 2 to be blended is 10 parts.

FIG. 1

TRANSMITTANCE (%)

⑲日本国特許庁（JP）　⑪特許出願公開

⑫公開特許公報（A）　平3−231954

⑤Int. Cl.⁵	識別記号	庁内整理番号
C 08 L 33/12	LJB	8016−4J
B 29 C 45/00		2111−4F
G 02 B 5/02	B	7542−2H
//(C 08 L 33/12 25:02)		

⑬公開　平成3年(1991)10月15日

審査請求　未請求　請求項の数 5　(全7頁)

⑭発明の名称　成形体用アクリル樹脂組成物、成形品およびその製造方法

⑳特　願　平2−29078
㉒出　願　平2(1990)2月7日

㉗発明者　川波　征一　新潟県北蒲原郡中条町倉敷町2番28号　株式会社クラレ内
㉗発明者　鈴木　吉郎　東京都中央区八丁堀2丁目9番1号　株式会社クラレ内
㉗発明者　伊藤　安太郎　新潟県北蒲原郡中条町倉敷町2番28号　株式会社クラレ内
㉗発明者　安中　雄次　新潟県北蒲原郡中条町倉敷町2番28号　株式会社クラレ内
㉑出願人　株式会社クラレ　岡山県倉敷市酒津1621番地
㉔代理人　弁理士　本多　堅

明　細　書

1．発明の名称

成形体用アクリル樹脂組成物、成形品およびその製造方法

2．特許請求の範囲

(1) メタクリル酸メチル系重合体100重量部に対して、芳香族ビニルモノマー50～99重量%および架橋性モノマー1～50重量%からなる平均粒子径1～15μmの架橋ポリマー微粒子を1～20重量部含有してなる成形体用アクリル樹脂組成物。

(2) 架橋ポリマー微粒子が粒径10μm未満の粒子を重量分布で60%以上含有する平均粒子径5～9μmの微粒子である請求項1記載の樹脂組成物。

(3) 請求項1又は2記載のアクリル樹脂組成物よりなるアクリル樹脂成形品。

(4) 請求項3記載の成形品からなる光学機器用拡散板。

(5) アクリル樹脂材料を射出成形して光拡散性及び艶消し性を有するアクリル樹脂成形品を得る方法において、請求項1又は2記載のアクリル樹脂組成物を艶消し加工の施こされていない成形型キャビティ内に射出成形することを特徴とするアクリル樹脂成形品の製造方法。

3．発明の詳細な説明

〔産業上の利用分野〕

本発明は成形体用アクリル樹脂組成物、成形品およびその製造法に関し、より詳しくは、光拡散性及び艶消し性に優れた成形体用アクリル樹脂組成物、該組成物を射出成形あるいは押出成形してなる高い光拡散性と良好な艶消し性とを有するアクリル樹脂成形品およびその製造方法に関する。

〔従来の技術〕

アクリル樹脂は照明カバー、ディスプレィ、看板等の光拡散性を必要とする種々の用途に用いられており、このような光拡散性アクリル樹脂としては従来(a)平均粒径10μm以下の硫酸バリウム、炭酸カルシウム、酸化チタン等の無機微粉末をアクリル樹脂中に含有せしめたもの（特開昭60−13

9758号公報）、(b)4～50μmのシリカ、ガラス、水酸化アルミニウム等の透明微粒子をアクリル樹脂中に分散せしめたもの（特開昭60-184559 号公報、特開昭61-4762 号公報）および(c)スチレン系樹脂又は粒子径30～500μmの架橋したスチレン－アルキルアクリレート系ポリマーをアクリル樹脂中に混合分散せしめたもの（特開昭56－36535 号公報、特開昭61-159440 号公報）などが知られている。

〔発明が解決しようとする課題〕

しかしながら、前記(a)，(b)の方法の如く無機微粒子を含有するアクリル樹脂の場合には十分に光拡散性を高めようとすると光線透過率が低下してしまうという欠点を有しており、また前記(c)の方法のようにスチレン系樹脂、粒子径30～500μmの架橋したスチレン－アルキルアクリレート系ポリマーを含有するアクリル樹脂の場合には光拡散効果は発現するものの完全拡散に近づけるにはやはり光線透過率が低下してしまったり、分散不良や流れ模様などの成形品外観の欠点が発生したり、あるいは表面の艶消し状態が十分でなかったりするなどの問題点を有しており、高い光線透過率と高い光拡散効果とを求める市場の要請に十分応えられないのが実情であった。特に近年普及がめざましいＯＡ機器、液晶ディスプレイ、バックライトパネル等の光学機器用光拡散板においてはその光線透過率、光拡散性の改善要望が強い。

したがって、本発明は、上記問題点を解決して完全拡散に近い高度の光拡散性を有する艶消性アクリル樹脂成形品を提供することを目的とする。

〔課題を解決するための手段〕

本発明者等は、前記課題を解決すべく光拡散剤の種類について鋭意研究を進めた結果、特定粒子径を有する架橋ポリスチレン重合体微粒子をメタクリル酸メチル系重合体に配合するのが有効であることを見出し、本発明を完成した。

すなわち、本発明によれば上記目的は、メタクリル酸メチル系重合体１００重量部に対して、芳香族ビニルモノマー５０～９９重量％および架橋性モノマー１～５０重量％からなる平均粒子径１～１５μmの架橋ポリマー微粒子を１～２０重量部含有してなる成形体用アクリル樹脂組成物、および該組成物よりなるアクリル樹脂成形品によって達成される。

また、上記目的は、アクリル樹脂材料を射出成形してアクリル樹脂成形品を得るに際し、上記アクリル樹脂組成物を艶消し加工の施こされていない成形型キャビティ内に射出成形することによって達成される。

以下本発明を詳細に説明する。

本発明でいうメタクリル酸メチル系重合体とは、メタクリル酸メチルホモポリマーまたはメタクリル酸メチルを８０％以上含むコポリマーをいい、紫外線吸収剤、熱安定剤、着色剤、無機微粉末等の微量添加剤は目的範囲内で含んでいることは、なんら差し支えない。また、その分子量は、特に本発明において制限されるものではないが、射出成形および押出成形時などの混練のしやすさあるいは物性面等から一般に５万乃至５０万、好ましくは、７万乃至３０万である。

本発明の架橋ポリマー微粒子は芳香族ビニルモノマーおよび架橋性モノマーを重合することによって得られる微粒子であるが、本発明の目的に支障を与えない範囲で他の共重合性モノマーを加えることもできる。

芳香族ビニルモノマーとしてはスチレン、α－メチルスチレン、ビニルトルエン、ハロゲン化スチレン等を用いることが可能であるが、スチレンが特に好ましい。該芳香族ビニルモノマーの使用量は５０～９９重量％、好ましくは８０～９５重量％の範囲である。

架橋性モノマーとしては分子内に２個以上の不飽和結合をもつ化合物が用いられ、その具体例としてはエチレングリコールジメタクリレート、ポリエチレングリコールジメタクリレート、1,4－ブタンジオールジメタクリレート、ネオペンチルグリコールなどの二官能性ジメタクリレートやジビニルベンゼン等の多価ビニルベンゼン等を好ましく挙げることができ、ジビニルベンゼンが特に好ましい。該架橋性モノマーの使用量は前モノマ

ーに対し１～５０重量％、好ましくは５～２０重量％の範囲である。

本発明に用いられる前記微粒子の粒径は１～４０μm、好ましくは１～２５μm、最も好ましくは１～１０μmであり、また平均粒子径は１～１５μm、好ましくは５～９μmの範囲であり、更に好ましい微粒子の態様としては、ポリマー微粒子粒径別含量の変動に対する光拡散性、艶消し表面外観への影響の観点から前記範囲において粒径１０μm未満の粒子が重量分布で６０％以上、好ましくは９０％以上を占めるものである。ここでいう平均粒子径とは、各粒径を重量積算し全重量の５０％にあたる粒径を意味し、たとえば重力沈降法により透過式粒度分布測定器（（株）セイシン企業製：SKA 5000）等により測定できる。光拡散状態の均一性及び風合いの点から懸濁重合による球状微粒子が好ましく使用され、粒径分布の狭い方が均一な光拡散性が得られるのでより好ましく使用される。これらの懸濁重合による微粒子としては特開昭64-26617号公報、特開平1-146910号公報、特開平1-172412号公報等で示された処方及び懸濁方法によって製造されたもの、あるいは市販のものとして積水化成品工業株式会社製：テクポリマーSBX-4，SBX-6，SBX-8，SBX-12（架橋ポリスチレン微小球状微粒子）などが使用できる。ポリマー微粒子の粒径が１μm未満の場合には透過光により赤っぽく見える傾向があり好ましくなく、一方４０μmを超える場合又は平均粒子径が１５μmを超える場合には完全拡散に近い高度の光拡散性を得ることができず好ましくない。また該微粒子の配合量は、メタクリル酸メチル系重合体１００重量部あたり１～２０重量部、好ましくは３～１０重量部である。その配合量が１重量部未満の場合には透けやすくなると共に十分な光拡散性を得ることができずまた表面の艶消し状態も十分でなく、一方２０重量部を超える場合には光線透過率が低下し、またこれ以上添加しても艶消し状態や光拡散性などが更に向上する効果は見られないので好ましくない。

このようにして得られた架橋ポリマー微粒子は、

十分な光拡散性を得る目的からゲル含有量の値が９５％以上でかつ膨潤度が２以下であることが好ましい。ゲル含有量が９５％未満の場合、又は膨潤度が２を超える場合には混練時粒子の粒径が変化し完全拡散に近い拡散性を得ることができないばかりか艶消し外観も均一にきめ細いものとならず好ましくない。

架橋ポリマーのゲル含有量、膨潤度の調整は架橋性モノマーの種類、量の調整および連鎖移動剤の使用により行うことができるが、前記通常行われる懸濁重合によりゲル含有量９５％以上、膨潤度２以下の架橋ポリマー微粒子を得ることができる。

本発明における光拡散性及び艶消し性にすぐれた成形体用アクリル樹脂組成物とは、メタクリル酸メチル系重合体１００重量部に対して前記架橋ポリマー微粒子を１～２０重量部含有するものであり、たとえばメタクリル酸メチル重合体および前記微粒子をヘンシェルミキサーなどで攪拌混合したものあるいは混合後押出機にかけてペレット状にしたものなどをいう。該組成物は安定に保存するためあるいは成形機への喰い込みを良くするためペレット状にしたものが好ましく用いられる。このような成形体用アクリル樹脂組成物は押出成形あるいは射出成形などの成形体用材料として使用されるが、押出成形では樹脂を押出した後の成形ロールとの接触状態により艶消し状態が左右されやすいため、このような問題のない射出成形に好適であり、射出成形に適し光拡散性及び艶消性に優れた成形体用アクリル樹脂組成物として好ましく使用される。

本発明における射出成形条件は本発明の本質的な構成要件ではなく、通常の射出成形機を用い通常の射出条件下で前記アクリル樹脂組成物を艶消し加工の施こされていない成形型キャビティに射出成形することにより、光拡散性及び艶消し性にすぐれたアクリル樹脂成形品を製造することができる。たとえば、前記メタクリル酸メチル重合体及び前記微粒子をヘンシルミキサーなどで攪拌混合したものあるいは混合後押出成形機にかけてペ

レット状にしたものを射出成形機で鏡面金型キャビティ内に射出成形することにより、従来のものでは決して得ることのできなかった。完全拡散に近い拡散性と均一で美麗な艶消し表面を有するアクリル樹脂成形品を得ることができる。

（実施例）

以下、実施例により本発明をさらに具体的に説明する。

なお、実施例、比較例における「%」および「部」はすべて「重量%」および「重量部」をそれぞれ表わし、また実施例および比較例により得られたアクリル樹脂成形品の性能および架橋ポリマー微粒子のゲル含有量、膨潤度は以下の方法により測定、評価した。

光線透過率およびヘイズ値

JIS K7105 に準拠して積分球式光線透過率測定装置（（株）村上色彩研究所製：ＲＭ－１５）により測定し、全光線透過率、ヘイズ値を算出した。

透過特性

変角光度計（（株）村上色彩研究所製：GP-1R）

を用い下記の光学条件により０°，５°，１０°，２０°，３０°，４０°，５０°，６０°，７０°，８０°，９０°の各角度について透過率を測定した。

光束：１２φm/m、

平行度：±0.5以下、

集光レンズ：有効口径１６m/m φ、

受光視野角：0.８６°、

受光スリット径：３m/m φ

分光条件：Ｃ光に対するCIE 比視感度に近似

表面状態

室内において蛍光灯を試料表面に反射させて目視観察し、試料の艶消し状態を次の記号で表わした。

◎…蛍光灯の輪郭は全く見えず均一美麗な艶消し表面である。

○…蛍光灯の輪郭が認められないかほとんど認められない。

△…蛍光灯の輪郭は認められるが不明瞭であり、表面の凹凸がある。

×…蛍光灯の輪郭が明瞭に認められ、表面の凹凸がほとんどない。

××…表面が荒れており、均一な艶消し状になっていない。

透け状態

１５Ｗの直管蛍光灯（ナショナル製：パルック）前方８cmの位置に試料片を平行に置き、更に該試料片から５０cm離れた位置で試料片を通して光源の輪郭が見えるかどうか目視観察し、次の記号で表わした。

○…蛍光灯の輪郭は認められない。

△…蛍光灯の輪郭がかすかに認められる。

×…蛍光灯の輪郭が明瞭に認められる。

ゲル含有量・膨潤度

所定量の架橋ポリマー微粒子を秤量ビンに秤量し、約１００倍量のメチルエチルケトン(MEK) 中に４８時間浸漬する。浸漬後余分のMEK をデカンテーションにより十分に除去しMEK で膨潤状態にある試料の重量を求める。ついで減圧乾燥によりMEK を乾燥し、試料の絶乾重量を求める。これに

より次式から算出する。

ゲル含有量（重量%）

$$= \frac{\text{絶乾重量（MEK 浸漬後）}}{\text{採取試料重量}} \times 100$$

$$\text{膨潤度} = \frac{\text{MEK 膨潤状態の試料の重量} - \text{絶乾重量}}{\text{絶乾重量}}$$

実施例１

５ℓのセパラブルフラスコに、懸濁分散剤としてポリビニルアルコール（（株）クラレ製PTA 420)18.37gを2625mℓの蒸留水に溶解させ、モノマー系としてスチレン５４０mℓ、ジビニルベンゼン６０mℓ、トルエン４００mℓ、ラウロイルパーオキサイド1200g の溶液を加えた。この混合液をラボディスパーザー（三田村理研（株）製Ｘ－1020型）を用い、顕微鏡で観察した粒径が最大のもので２５μmになるまで分散させた。フラスコに温度計、撹拌装置、冷却管をとりつけ、窒素気流下８０℃で６時間重合反応を行なった。得られたスラリーを吸引濾過し、濾別した微粒子を再び蒸留水に分散させて付着しているポリビニルアルコー

ルを洗浄し濾過した。これを１００℃で２日間真空乾燥して希釈剤のトルエンを蒸発させた後、粒径を透過式粒度分布測定器（（株）セイシン企業製：SKA5000)で測定したところ粒径が２～２５μm、平均粒子径８μm（１０μm未満の粒子は重量分布で６５％）の架橋ポリマー微粒子を得た。この微粒子のゲル含有量は９８％、膨潤度は１以下であった。得られた微粒子をアクリル酸メチル５％を含有するメタクリル酸メチル重合体（（株）クラレ製：パラピーズ）１００部に対して５部添加し、ヘンシェルミキサーで混合撹拌の後、押出機（中央機械製作所製：VSK-40）で押出してペレット化し、このペレットを射出成形機（東芝機械（株）製：IS-25Zp)により成形温度２００～240℃、金型温度５０℃の条件で鏡面キャビティー内に射出成形し、厚さ２㎜の平板成形品を得た。

この成形品の性能評価の結果を第１表に示すが高光拡散性の良好な艶消し表面を有するアクリル樹脂成形品が得られた。

実施例２～４

下記組成及び粒径の架橋ポリマー微粒子を各種添加量で添加する以外は実施例１と同様にしてペレット化及び射出成形し厚さ２㎜の平板成形品を得た。これらの成形品の性能評価の結果を第１表に示す。

実施例No.	組　成	粒　径
2	スチレン 95 部 ジビニル 5 部 ベンゼン	粒径１～10μm、平均粒子径４μm 10μm未満の粒子：重量分布で97％
3	同　上	粒径１～16μm、平均粒子径６μm 10μm未満の粒子：重量分布で91％、ゲル含有量96％、膨潤度1.1
4	同　上	粒径２～64μm、平均粒子径12μm 10μm未満の粒子：重量分布で30％

比較例１，２

下記組成及び粒径の架橋ポリマー微粒子を各種添加量で添加する以外は実施例１と同様にしてペレット化及び射出成形し厚さ２㎜の平板成形品を得た。これらの成形品の性能評価結果を第１表に示す。

比較例No.	組　成	粒　径
1	スチレン 95 部 ジビニル 5 部 ベンゼル	粒径２～64μm、平均粒子径22μm 10μm未満の粒子：重量分布で５％
2	同　上	粒径12～200μm、 平均粒子径50μm

平均粒子径５０μmのものは、樹脂の充填速度が速い場合大きい粒子による流れ模様が出やすい傾向が見られるほか、成形品表面が均一の艶消し状とならず、また光拡散性も劣っていた。

比較例３

アクリル酸メチル５％を含有するメタクリル酸メチル重合体１００部に対して、1.0～２０μmの粒度分布を有し平均粒子径６μm（１０μm未満の粒子は重量分布で９０％）のポリスチレン微粒子を１部、３部、５部、１０部それぞれ添加しヘンシェルミキサーで混合撹拌の後、実施例１と同様に厚さ２㎜の平板成形品を得た。これらの性能評価結果を第１表に示すが、高拡散で高光線透過率の成形品は得られず、又添加量が少くない時は成形品に分散不良があり、添加量が多いと貝がら模様が発生した。

比較例４

比較例３で用いたメタクリル酸メチル重合体１００部に対して、３～３０μmの粒度分布を有し平均粒子径１０μmのポリスチレン微粒子（積水化成品工業（株）製：テクポリマーＳＢ－１０）を0.５部、１部、５部、１０部それぞれ添加しヘンシェルミキサーで混合撹拌の後、実施例１と同様にして厚さ２㎜の平板成形品を得た。これらは高拡散で高光線透過率の成形品は得られず、比較例３と同様に分散不良、貝がら模様が発生した。

以下余白

第 1 表

	微粒子配合量(部)	全光線透過率(%)	ヘイズ(%)	透過特性 透過光の角度分布（0°方向を100とする%） 0°	10°	30°	40°	60°	70°	表面状態	透明状態	備考
実施例1	5	57	94	100	99	90	81	52	32	◎	○	
実施例2	1	71	95	100	96	69	53	27	16	△	○	
	3	57	94	〃	99	90	81	52	32	○	○	
	5	48	〃	〃	〃	92	84	55	34	◎	○	
	10	40	95	〃	〃	〃	〃	〃	〃	◎	○	
	30	39	94	〃	〃	〃	〃	54	〃	◎	○	
実施例3	1	74	94	100	93	58	41	19	11	○	○	
	3	59	〃	〃	99	89	80	51	31	◎	○	
	5	55	93	〃	〃	92	83	54	34	◎	○	
	10	45	95	〃	〃	〃	84	50	28	◎	○	
	30	30	94	〃	〃	〃	83	52	31	◎	○	
実施例4	1	80	93	100	43	13	8	3	1	△	○	
	3	65	95	〃	97	76	62	33	17	○	○	
	5	58	〃	〃	99	88	79	47	26	○	○	
	10	50	〃	〃	〃	92	83	50	28	◎	○	
	30	37	94	〃	〃	〃	82	〃	〃	◎	○	
比較例1	1	82	89	100	4	1	0	0	0	△	△	
	3	69	94	〃	91	57	42	20	10	△	○	
	5	60	95	〃	98	84	72	41	20	△	○	
	10	52	94	〃	99	91	83	50	28	○	○	
	30	37	〃	〃	〃	〃	82	48	27	◎	○	
比較例2	1	86	65	100	0	0	0	0	0	×	×	
	3	79	90	〃	10	2	1	0	0	××	△	
	5	74	94	〃	51	20	13	5	3	××	○	
	10	64	95	〃	96	71	57	30	15	××	○	
比較例3	1	52	94	100	0	0	0	0	0	×	×	分散不良有
	3	37	〃	〃	72	65	58	37	23	×	○	
	5	31	〃	〃	99	90	82	53	33	×	○	
	10	19	95	〃	〃	93	84	55	35	×	○	貝ガラ模様有
比較例4	0.5	69	52	100	0	0	0	0	0	×	×	分散不良有
	1	55	89	〃	1	1	0	0	0	×	×	〃 〃
	5	30	94	〃	99	92	84	53	30	×	○	貝ガラ模様有
	10	21	〃	〃	〃	93	86	55	31	×	○	〃 〃

〔発明の効果〕

本発明は以上説明したように、メタクリル酸メチル系重合体１００重量部に対して、芳香族ビニルモノマー５０～９９重量％および架橋性モノマー１～５０重量％からなる平均粒子径１～１５μmの架橋ポリマー微粒子を１部～２０重量部含有してなる光拡散性及び艶消性にすぐれた成形体用アクリル樹脂組成物であるから、配合するポリマー微粒子の粒径および添加量により光拡散性および艶消し状態を変化させることができるので、簡便に種々の光拡散性、艶消し性を有する成形体用の組成物を提供することができ、特に量産性にすぐれた射出成形材料として有用である。

また、上記成形体用アクリル樹脂組成物を押出成形又は射出成形してなる光拡散性及び艶消し性に優れたアクリル樹脂成型品であるから、大量に安価に供給できると共に種々の光拡散性及び艶消し性を有する照明カバー、ディスプレー、グレージング、計器カバー等として有用であり、特に近年普及がめざましいＯＡ機器、液晶ディスプレイ、バックライトパネル等の光学機器用光拡散板として好適である。

更に本発明は、上記アクリル樹脂組成物を成形型キャビティ内に射出成形する光拡散性及び艶消し性に優れたアクリル樹脂成形品の製造方法であるから、キャビティ面を微細に加工するとか、十分に鏡面に研磨する必要がなく安価に金型を製作することができ、また１つの型で成型材料を変えることにより種々の光拡散性及び艶消し性に優れた成形品を製造することができ、分散不良や貝がら模様の発生が皆無であるので、安価、簡便に光拡散性及び艶消し性に優れたアクリル樹脂成型品を提供することができ有利である。

４．図面の簡単な説明

第１図は、実施例１（Ａ）、実施例２の微粒子配合量３部（Ｂ）、実施例３の微粒子配合量３部（Ｃ）、実施例４の微粒子配合量５部（Ｄ）、比較例１の微粒子配合量５部（Ｅ）および比較例２の微粒子配合量１０部（Ｆ）の透過特性をそれぞれ表わした図である。

第１図